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**THE EFFECT OF THERMAL TREATMENT ON THE INTERFACE STRENGTH
IN GRAPHITE/POLYCARBONATE COMPOSITES**

BY

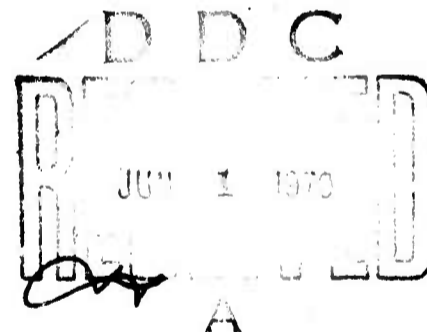
F. S. CHENG, J. L. KARDOS AND T. L. TOLBERT

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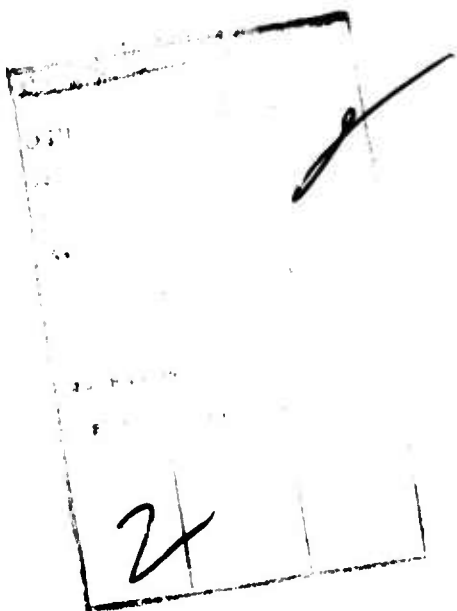
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IN GRAPHITE/POLYCARBONATE COMPOSITES

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February 1970

Program Manager
Rolf Buchdahl

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FOREWORD

The research reported herein was conducted by the staff of the Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0214 (formerly N00014-66-C-0045), ARPA Order No. 876, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites."

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THE EFFECT OF THERMAL TREATMENT ON THE INTERFACE STRENGTH IN GRAPHITE/POLYCARBONATE COMPOSITES

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Abstract

Pronounced effects of thermal treatment on the properties of graphite/polycarbonate composites have been demonstrated and studied. At a 20 percent volume loading of random-in-a-plane, discontinuous fibers, both specimen strength and modulus were found to be very sensitive to initial molding temperature and to subsequent heat treatments. Scanning electron micrographs of tensile fracture surfaces show that the matrix adheres to the fibers more tenaciously and in greater quantities as the tensile strength increases. Preliminary diffraction evidence indicates that the polycarbonate has epitaxially crystallized on and around the graphite fibers in the case of the annealed samples. The increases in composite strength are attributed to increases in interface strength which arise from better wetting and partial crystallization at the interface.

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Introduction

Over the past few years graphite fibers have been developed to a point that they now can compete with, and in some aspects surpass, glass fibers as reinforcing agents. In addition to replacing glass in thermosetting systems such as filament wound epoxy composites, graphite fibers are beginning to be employed as a discontinuous reinforcement for thermoplastics [1]. This is a particularly advantageous combination in that the very high specific properties normally achieved only with reinforced thermosets can be obtained in these systems without the usual sacrifice in processability.

The level of crystallinity in a number of so-called high temperature thermoplastics, such as polycarbonate and polysulfone, is quite low under most circumstances. However, under certain conditions these materials can be made to crystallize and thereby to change markedly in bulk properties. For example, the stiffness of polycarbonate resin can be increased 50 percent or more by simply holding it at a temperature above which melting occurs; increases of 10 degrees in heat deflection temperature are not uncommon under these conditions. Crystallinity also can be promoted by exposure to certain solvent environments [2, 3] or by introducing nucleating sites in the form of a filler or substrate [4].

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Graphite fibers present a relatively high-energy surface which should be ideal for nucleating or "promoting" crystallization in such systems; in fact, graphite has been reported to contribute to epitaxial crystallization of hexamethylene-diammonium adipate [5] and polyethylene [6].

This raises the possibility that one might be able to tailor the interface in a graphite/thermoplastic composite and improve performances of the system by subjecting it to controlled thermal treatment which will cause the matrix to crystallize epitaxially on and around the fiber. The result would be improved fiber/matrix bonding brought about by generation of a transition region of intermediate modulus around the fiber, which should permit more efficient transmission of stresses and therefore higher composite strength. Improvements in composite properties have in fact been achieved this way. We have been able to change the character of the interface and improve the properties of graphite/polycarbonate composites, for example, by simply varying thermal conditions during fabrication. This report summarizes initial results from studies on changes in composite mechanical properties and fracture surface morphology due to such variations.

Experimental

Two types of graphite fibers, Thornel 40 (Union Carbide Corporation, modulus - 36.5×10^6 psi, strength - 203×10^3 psi) sized with polyvinyl alcohol and Hercules HMG (modulus - 56×10^6 psi, strength - 300×10^3 psi) sized with Epon 828, were used in this study. The fibers were cut into 1/8 inch lengths and sonically dispersed in a 75 percent methanol-25 percent water solution along with 60-100 mesh polycarbonate powder (General Electric Lexan 145). A preform mat of two-dimensionally random fibers

uniformly mixed with resin powder was prepared from the suspension by draining off the solution through a filter shaped like the final sample (5" x 1/2" x 1/16" plate) in the bottom of the container. The matt was dried at 110°C for eight hours under vacuum and then compression molded. Molding was carried out at 5000 psi using various temperature cycles. After heating the fiber/resin mixture under pressure to the molding temperature, specimens were (1) held at 190°C for 10 minutes and then slowly cooled to room temperature, (2) held at 275°C for 10 minutes and cooled, or (3) held at 275°C for 10 minutes and then annealed for three hours at 245°C before cooling. A total of 12 specimens were prepared under each regime. An equal number of unfilled bars of the same geometry molded under the same conditions was prepared as standards. Specimens were characterized by dynamic mechanical measurements, tensile stress-strain tests, and scanning electron microscopy (tensile fracture surfaces).

Results and Discussion

Tensile data for both unfilled and Hercules fiber filled specimens are shown in Table I. Note that only relatively minor changes in tensile mechanical properties were observed for the pure matrix specimens regardless of the treatment used. Dramatic changes in the properties of the reinforced specimens were observed, however. At 20 volume percent fiber loading, specimen strength and modulus were found to be very sensitive both to initial molding temperature and to subsequent annealing treatments. For example, the tensile strength of specimens reinforced with Hercules fiber was nearly doubled by changing the thermal history from molding the specimen at 190°C (25°C above T_g) to molding at 275°C and annealing at 245°C. Since the thermal treatment

used here should not affect the fibers themselves and the effect on unfilled resin properties is small, the fibers must have in some way contributed to or promoted changes in the matrix during thermal treatment. Similar, though slightly smaller, effects were observed in the Thornel 40 reinforced system.

Figures 1 to 3 are scanning electron micrographs of exposed Thornel fibers on tensile fracture surfaces of samples molded under three different conditions. For comparison, in Figure 4 we show a micrograph of the surface of a Thornel fiber "as-received." Note the similarity of this fiber to that shown in the micrographs of the composite molded at 190°C; this at least implies that the degree of adhesion in the 190°C composite is quite low. In fact it is clear that, in progressing from the 190°C treatment to molding at 275°C and then to preparation of samples at 275°C and annealing them, changes occur which result in more and more polymer matrix left adhering to the graphite after fracture. The same phenomenon occurs in the Hercules samples. Figure 5 shows the marked increase in adhering polymer from relatively bare fibers resulting from the 190°C treatment to fibers from samples which had been fabricated at 275°C and then annealed at 245°C. Again the implication is that the strength of the fiber/matrix bond is increasing. In each case the increase in the amount of polymer adhering to the fibers after fracture corresponds to increases in both tensile strength and tensile modulus. A similar trend was reported previously for glass-filled polyphenylene oxide [7] and glass filled epoxy systems [8], where the interface strength was varied experimentally with the use of coupling and release agents. It seems likely therefore that increased composite strength in the polycarbonate/graphite fiber system arises directly from increased interface strength and is therefore a function of better wetting and adhesion.

In light of References 5 and 6, it is likely that crystallization phenomena are involved in the mechanism for improved adhesion. There are also several experimental indications that the resin may be epitaxially crystallizing on and near the graphite surfaces. For example, strengthening has been observed to occur only when the fabrication temperature is above the normal melting point of crystalline polycarbonate, in this case about 265°C. Melting of any microcrystalline regions should not only permit better wetting of the fiber surface but also promote redevelopment of crystallinity at favored nucleation sites on the graphite surface [5, 6]. Furthermore, we have obtained limited transmission electron diffraction evidence from detachment replicas of the fibers at the fracture surfaces in the annealed samples, which indicate that oriented polycarbonate is present on the fiber surfaces. Discrete arcs corresponding to polycarbonate unit-cell spacings rapidly disappeared when the very low beam current was increased, even when a cold stage was employed, indicating that the polymer melted in the heat of the beam. High magnification scanning electron micrographs of the fiber surfaces in the annealed samples and those molded at 275°C often reveal polymer particles which appear to have an angular morphology such as can be seen in Figure 6. It is possible, of course, that oriented material could arise from deformation orientation during fracture as well as from crystallization. This seems unlikely, however, especially in light of the fact that the glass transition temperature of the matrix in all of the composites, as determined by non-destructive torsion pendulum measurements, is from 10 to 13°C above that of the unfilled polymer molded under the same conditions (see Table I); again, this indicates a considerable effect of the fiber surface on order developed within the matrix material. At this point we do not know to what extent the sizing material participates in the

strengthening mechanism. Limited results from samples containing size-free fibers indicate that the sizing is not responsible for the large increases observed, although sized fibers do seem to yield slightly stronger composites. A systematic study of the nature of the interface in this system is still underway and more detailed results will be presented in the near future.

Acknowledgment

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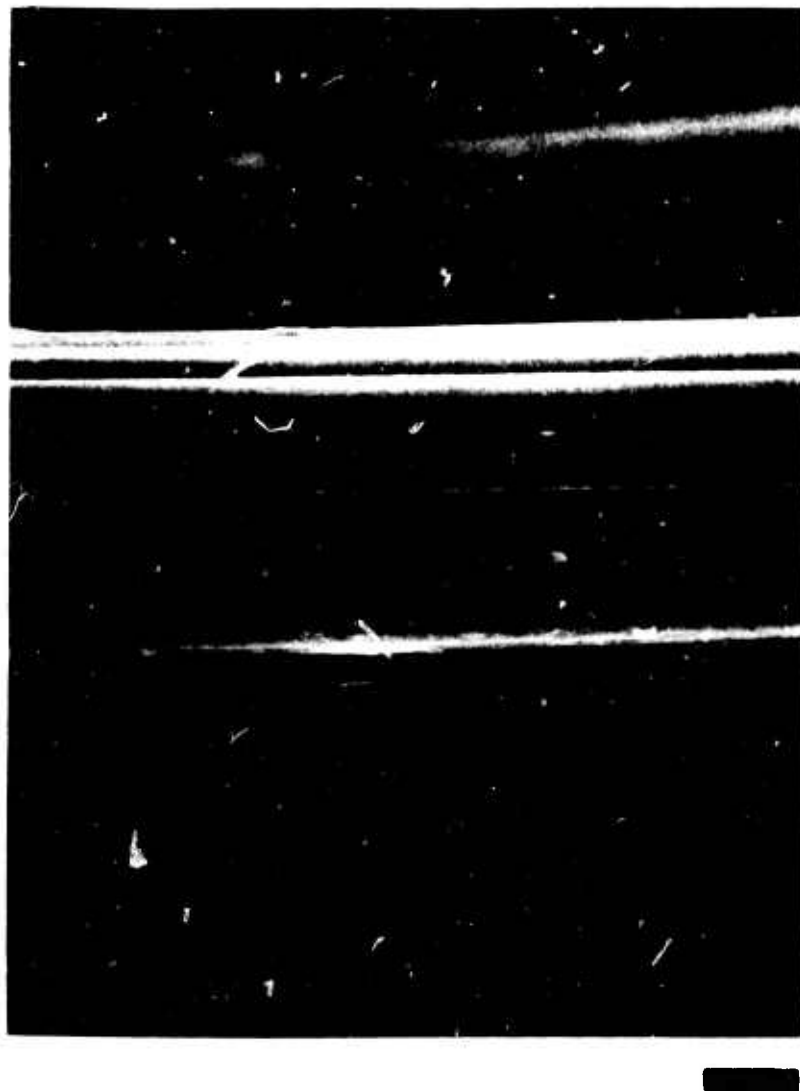


Figure 1. Scanning electron micrograph of exposed Thornel fiber on the tensile fracture surface of a sample molded at 190°C. Note the similarity of this fiber's surface to that of the "as-received" fiber in Figure 4. The scale bar represents 2 microns.



Figure 2. Scanning electron micrograph of exposed Thornel fiber on the tensile fracture surface of a sample molded at 275°C. Note the increase in adhering matrix on the fiber over that seen in Figure 1. The scale bar represents 2 microns.

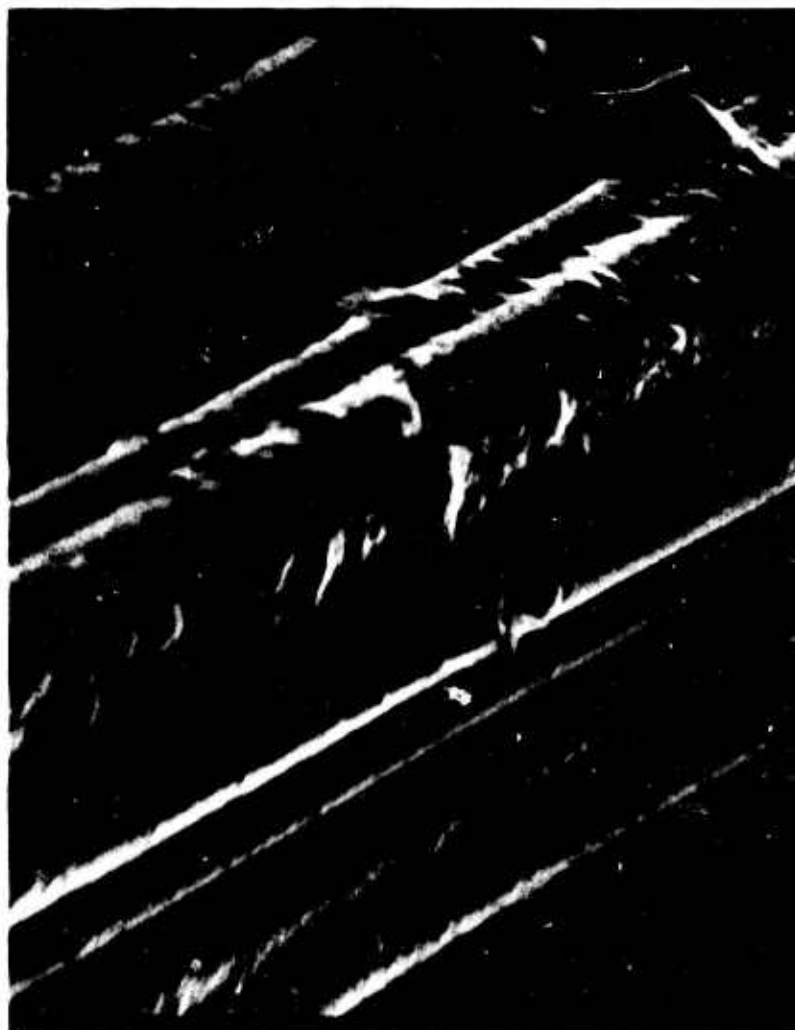
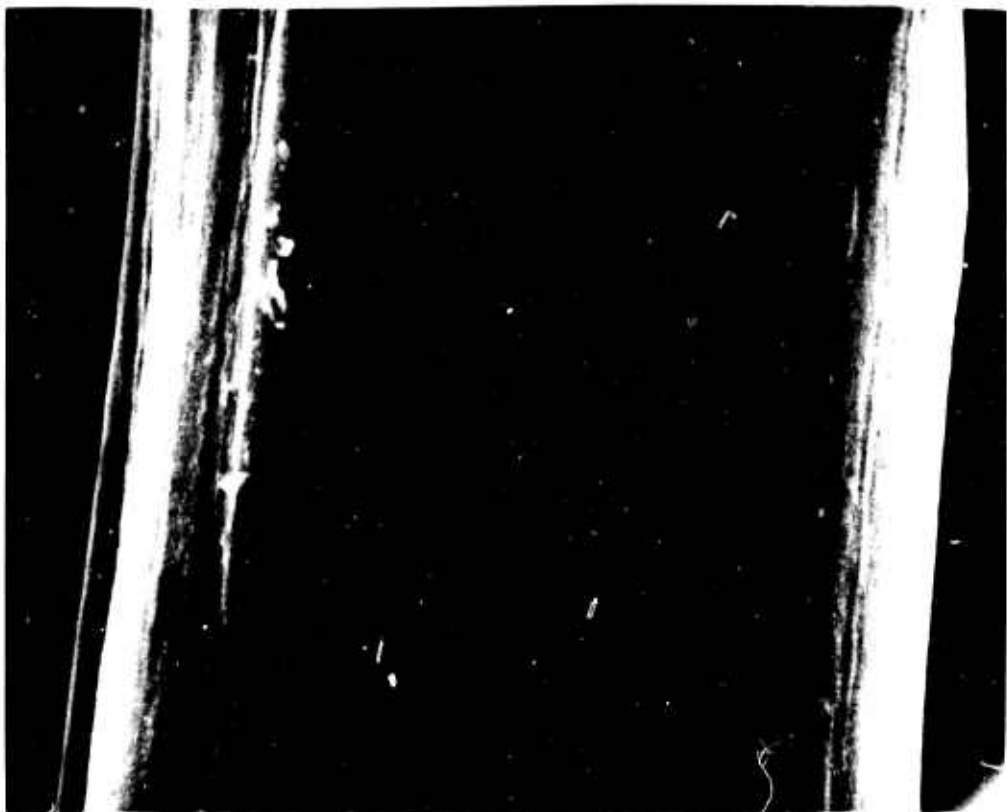


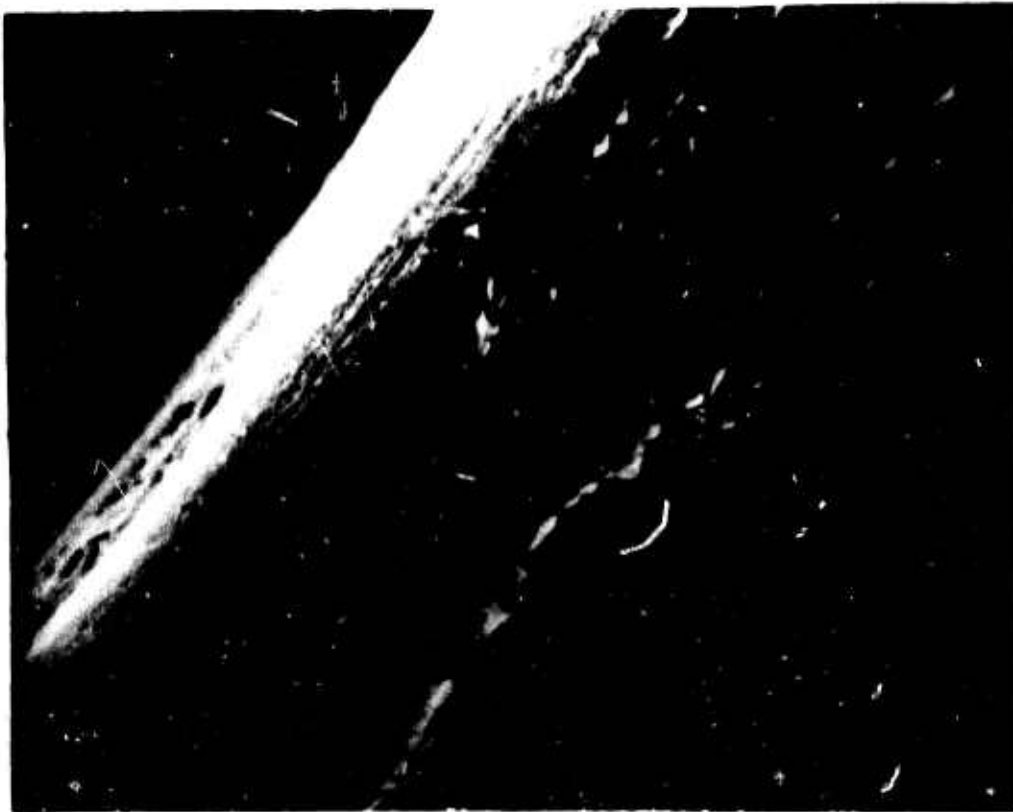
Figure 3. Scanning electron micrograph of exposed Thornel fiber on the tensile fracture surface of a sample molded at 275°C and then annealed at 245°C for three hours. Note the coating of matrix which almost completely covers the fiber. The scale bar represents 2 microns.



Figure 4. Scanning electron micrograph of an "as-received" Thornel fiber. The scale bar represents 2 microns.



A



B

Figure 5. Scanning electron micrographs of exposed Hercules fibers on the tensile fracture surface of samples (A) molded at 190°C and (B) molded at 275°C and then annealed at 245°C for three hours. Note the increase in amount of adhering plastic from (A) to (B). The scale bar represents 2 microns.



Figure 6. High magnification scanning electron micrograph of a Thornel fiber surface in the annealed sample. The adhering polymer particles appear to have an angular morphology characteristic of polymer crystals. The scale bar indicates 1 micron.

TABLE I

EFFECT OF THERMAL TREATMENT ON PROPERTIES OF
DISCONTINUOUS GRAPHITE/POLYCARBONATE COMPOSITES

Property	Thermal Treatment		
	190°C	275°C	275°C Annealed at 245°C
Tensile Strength ($\times 10^3$) psi			
Unfilled	8.3	8.6	8.2
Filled	8.6	13.7	16.3
% Strain			
Unfilled	5.1	6.2	2.8
Filled	0.79	0.84	0.76
Tensile Modulus ($\times 10^6$) psi			
Unfilled	0.32	0.34	0.57
Filled	1.93	2.90	3.78
Glass Transition Temperature, T_g , °C			
Unfilled	154	155	157-159
Filled	167-169	167-168	168

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Graphite/polycarbonate composites						
Interfaces						
Thermal treatment						
Annealing						
Strength						
Stiffness						
Crystallinity						
Scanning electron microscopy						
Glass transition temperature						